

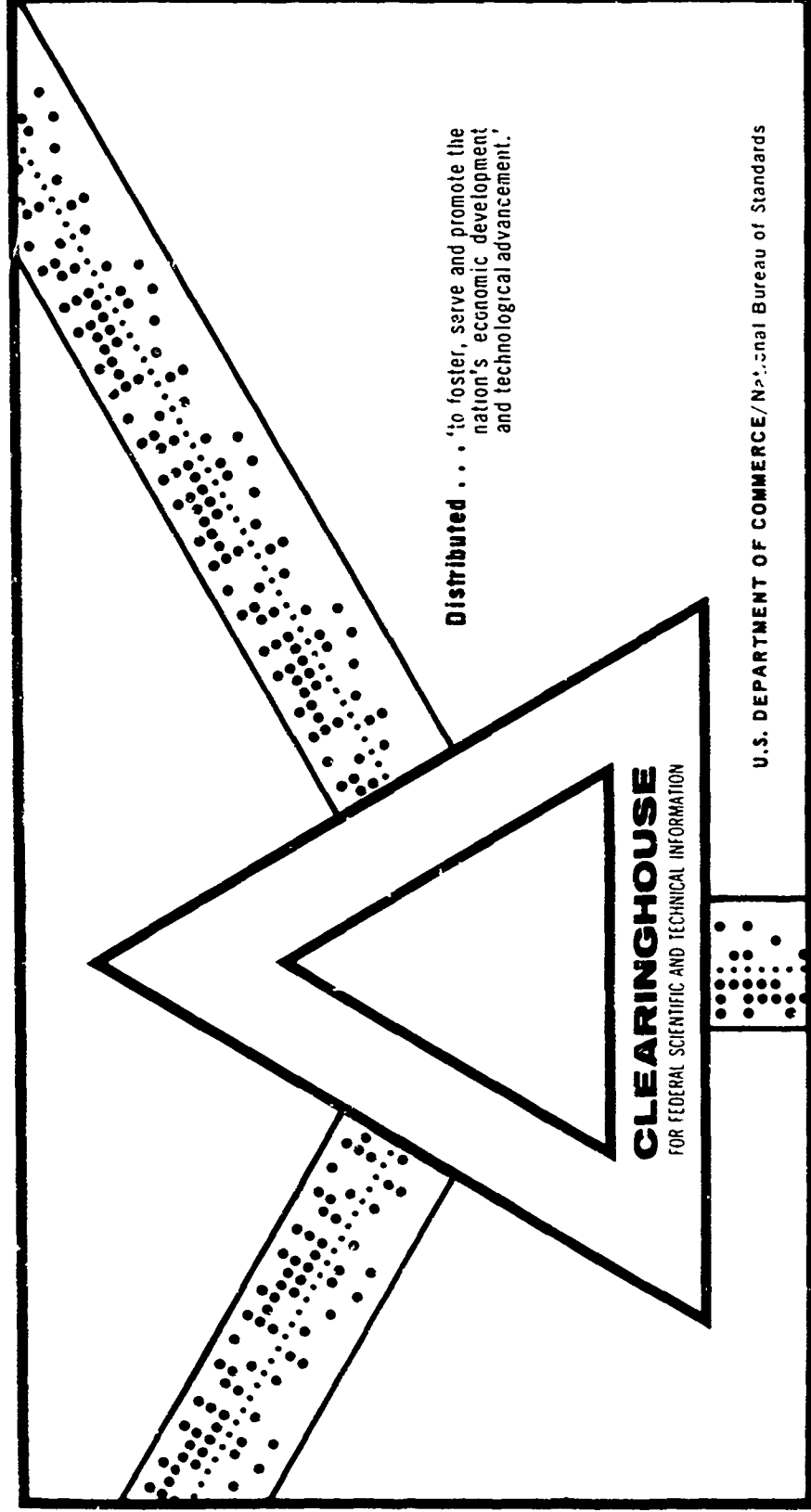
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STUDIES OF HIGH STRENGTH POLYPROPYLENE: THE ORIGINS OF
DYNAMIC RESPONSES

T. Waller George

North Carolina State University
Raleigh, North Carolina

November 1969



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Technical Report 69-9

November 1969

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T. Waller George

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Abstract

The report outlines research undertaken to identify a set of microstructure elements present in strong organic fiber in which reside the primary means of response on the part of the material to dynamic load application. The elements involve two microfibrillar concepts, viz., a set of nearly parallel structures and a set of finer transition fibrils which bridge between the former under conditions of nearly axial alignment. Scanning electron micrographs of the structural features are reported. The transition fibril is reported in one experimental setting to exhibit evidences of a labile chemical structure under exposure to ultraviolet radiation in the presence of halogens (room temperature).

Publication activity is reviewed and abstracts presented in the Appendix.

A second principal contribution involves the statistical theory of the strength of a parallel array of fiber. The model envisions individual filaments possessing strength properties distributed along the length in accordance with the conventional weakest-link hypothesis. A set of moment inequalities has been obtained which shows the mean bundle strength per element in the absence of interaction between the constituent elements to be progressively degraded as the bundle size increases. A finite asymptotic limit is obtained as the number of elements approaches infinity. Similar inequalities and limits have been obtained for higher moments of the underlying distributions describing bundle strength. Physical evidence of tie elements suggests the need for statistical studies of bundles containing interaction between elements. Some speculative discussion of the role of this interaction in determining practical bundle strength under dynamic and low temperature conditions concludes the report.

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STUDIES OF HIGH STRENGTH POLYPROPYLENE: THE ORIGINS OF DYNAMIC RESPONSES

The unitary fine structure of a synthetic fiber is itself composed of a fiber-like structure. This is a ribbon-like, fibrillar structure which in turn is composed of a more or less ordered arrangement of the constituent macromolecules. It is at the present unclear whether the stable microfibrillar unit is predominantly extend chain ordered or composed of some essential portion of fold chain crystalline structure. The study of the character of solid fibrillar matter derived from polymer melts, dopes, spinning solutions and the like provides a major challenge to the fiber scientist which has been recognized since the time of Staudinger who was probably the first to observe the fibrillar character of linear polymer upon transformation to the solid state from melts or various solution types.

The mechanical response of the arrangement of the microfibrillar set to tractions applied to the ends of macrofiber section constitutes the macroscopic response of the single filament. In principle, if the detailed structure of the array of microfibrillar elements is known together with the response patterns to applied tractions, one may envision the evolution of the pattern of mean fiber response to a given applied set of tractions. It has been an underlying premise of this work to seek to describe a set of strength elements (microfibrillar array) and study its control of the levels of observed macro strength of the monofilament.

In 1962 Ogle reviewed a wide set of papers reporting measurements of the transverse dimensions of microfibrillar-like structures in fibers made from the

commercially interesting linear fiber forming polymers and linear polyethylene. He adduced evidence for considering the structural element diameter in terms of close packing of seven smaller cylindrical structures. The first structure he proposed was an extended chain ordered cylinder composed of seven molecules. This basic unit was then compounded in groups of seven to make the second configuration, and so on. The first compound radial structure has not been observed as frequently as members of the higher associations. Nonetheless, it is notable that Heyn obtained such a dimension from careful studies of highly oriented ultrastrong ($\sim 8-9$ g/d) regenerated cellulose acetate (Fortisan). His technique was rather impressive. It involved a Fourier analysis of the radial small angle X-ray scattering of the fiber. The analysis was confirmed by companion studies of progressively swollen fibers wherein the regions around the compressed microfiber were loosened by a group of well known swelling agents, long known to be specific to the attack of cellulose in the chemically "accessible" regions of the fiber.

This report discloses work over the period 1967 to September 1969 during which the author and Themis Fellows, Paul A. Tucker, Jr., Moon Suh and Yeun-Jong Chou contributed to Task III of Contract No. N00014-68-A-0187, the NCSU Themis project on The Dynamic Response of Materials. During the period two papers were prepared for oral presentation: "Tensile Failure of Bundles of Nearly Parallel Filaments," presented at the Synthetic Fiber Symposium, Williamsburg, Virginia, April 19-21, 1968; and "Statistical Nature of Breakage in Bundles," presented at the Fourth Annual Symposium on High Performance Composites, St. Louis, Missouri, April 7-10, 1969. Dr. Moon Suh completed his dissertation, "A Study of the Distribution and Moments of Bundle Strength in

Sequential Breakage of Parallel Filaments." A brief note was prepared by Roper and George on a variant of the usual melt extrusion process which was found useful in producing ultratenacity polypropylene fiber. Finally, the senior investigator completed a manuscript which extended the first paper above to a point where publication was possible. Lastly, Yeun-Jong Chou completed his Master of Science thesis on "Inhomogeneous Deformation of Nylon 6,6." A portion of this work forms the basis of a third paper "The Mechano-Chemistry of Nylon 6,6 Fiber Yield Point" which is scheduled for presentation at the Richmond meeting of the American Chemical Society in November 1969.

The termination of the efforts on this project as of September 1969, at the request of the sponsor, resulted in much of the work originally envisioned only partially completed. The following sections contain reviewing statements concerning the progress achieved to the date of termination of the study.

The Point of View of the Study

The ultimate goal of the work was to achieve a new level of understanding of the origin and limits to the magnitude of the ultimate dynamic strength achievable in strong organic fiber. Polypropylene was taken as a major model for experimental study. To do this a new combined theoretical and operational description of the set of strength elements (both dynamic and static) was undertaken. This focused upon the ultimate fibrillar character of the highly oriented polypropylene fiber. Since the fibrillar nature of the fiber product arises itself in elements of the controlled fiber forming process, the work of necessity focused at first on the development of melt extrusion process capable of producing strong fibers. Such a process, somewhat different from present commercial processes

was delineated and described briefly by Roper and George. As delineated, the process produced a troublesome irregular diameter (denier) of fiber and yarn. In a paper recently submitted for publication the author shows this irregular denier is characterized by stochastic oscillations about the mean (stationary) denier. Further, if these denier irregularities could be removed by appropriate control, one may plausibly suppose the mean tensile properties of the fiber would be enhanced. Regions of high denier are associated with regions of low static strength.

The property irregularity noted above is doubtless reflected in the microscopic nature of the monofilament. A peeling technique originated by Scott several years ago has shown certain over-all micro features of strong polypropylene. These, as seen in stereoscanning electron microscope at magnification of about X35,000, are reproduced in Figures 1, 2 and 3. The first shows the manner in which the fiber is separated by the peel. The microfibrillar elements are clearly evident. Figures 2 and 3 show features of the finer axially aligned fibrils which have a diameter of the order of 200 \AA not completely resolved in the reproductions. A second more or less transverse structure is also visible in these figures. This structure is a transition region involving molecules with portions anchored in adjacent microfibrillar structures. Further discussion of this finding is given below.

Yarn and Filament Denier Irregularity

The paper referred to above shows the typical denier irregularity of melt spun polypropylene may be described by a correlogram and associated power spectrum as shown in Figures 4 and 5, respectively. The former refers to a sequence of 150 denier measurements made on 15 cm lengths each 60 cm of an



Figure 1. A split polypropylene monofilament showing a range of microfibrillar structures including "ribbons" (X10,000 original)



Figure 2. Detail of microfibrillar structure, polypropylene melt extruded. Note existence of incompletely resolved tie structure. The fiber axis is vertical. (X10,000 original)

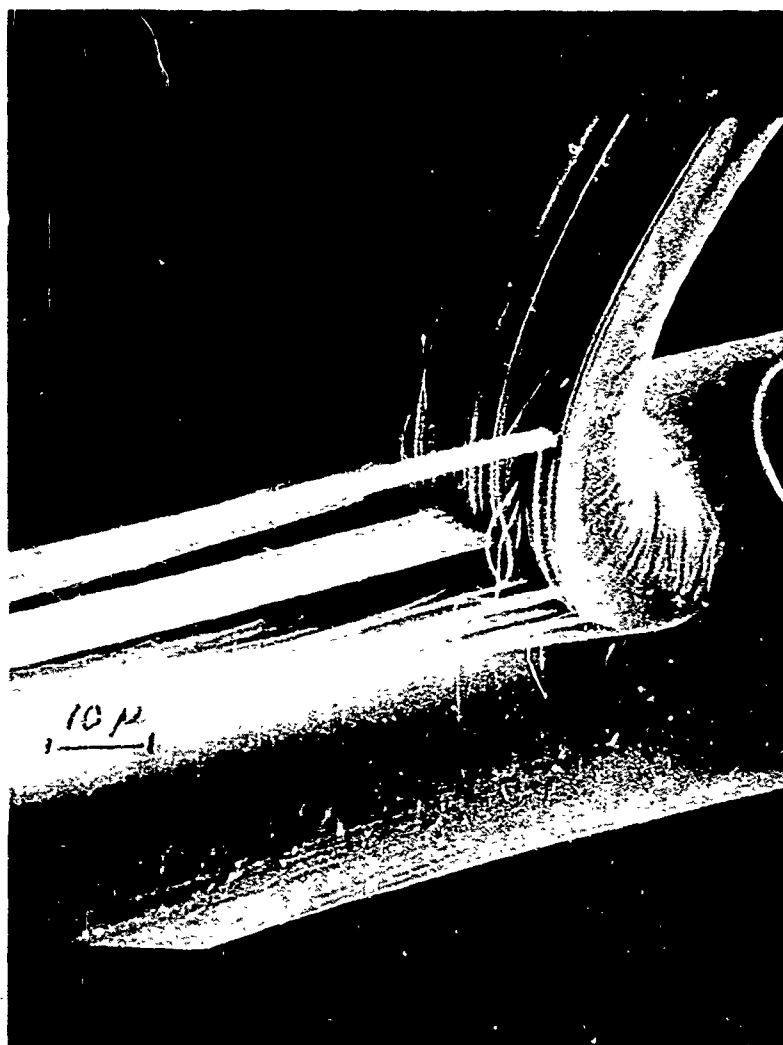


Figure 3. Complex tie structure including broken regions — melt extruded polypropylene. Fiber axis generally vertical. (X10,000 original)

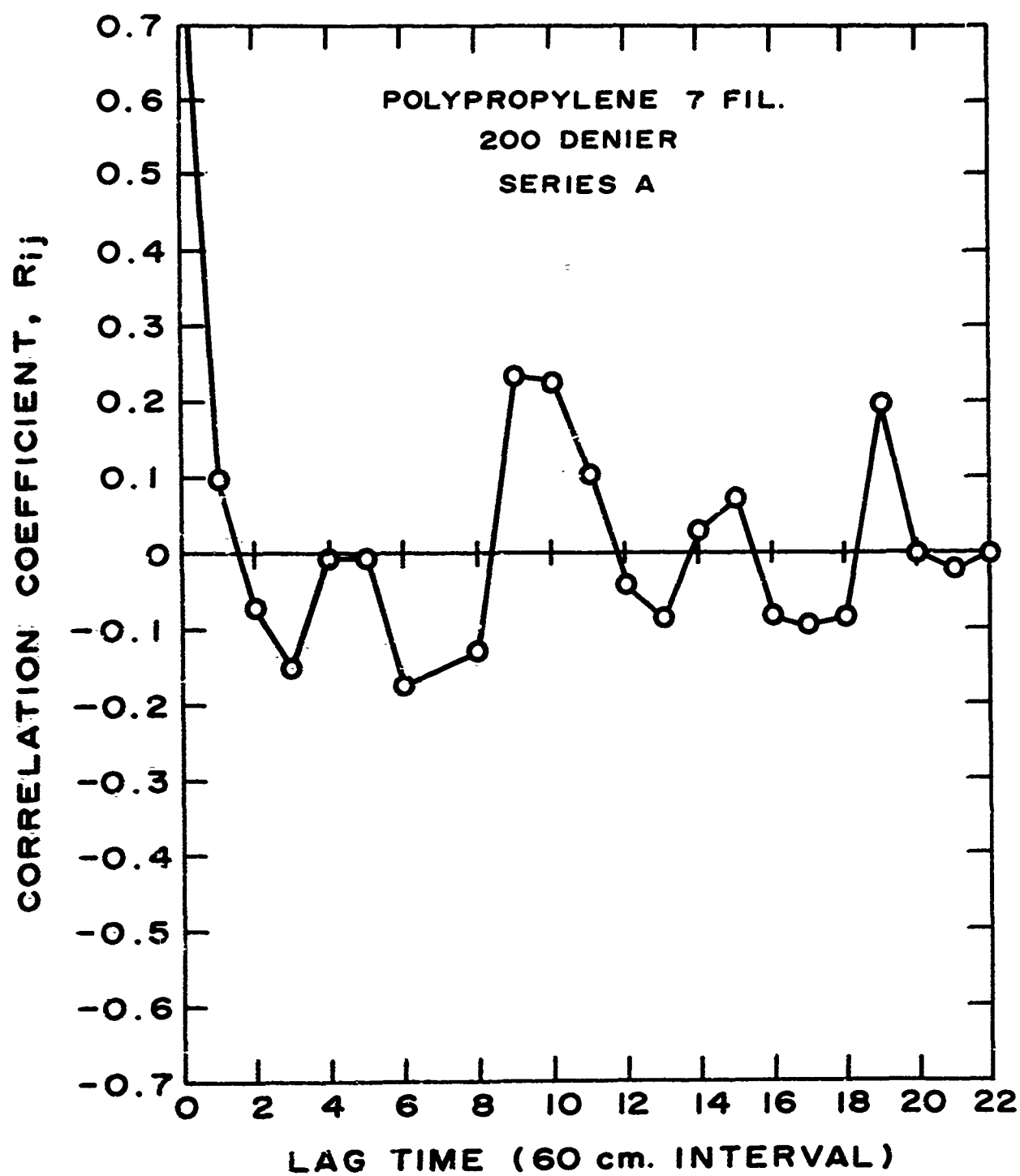


FIGURE 4

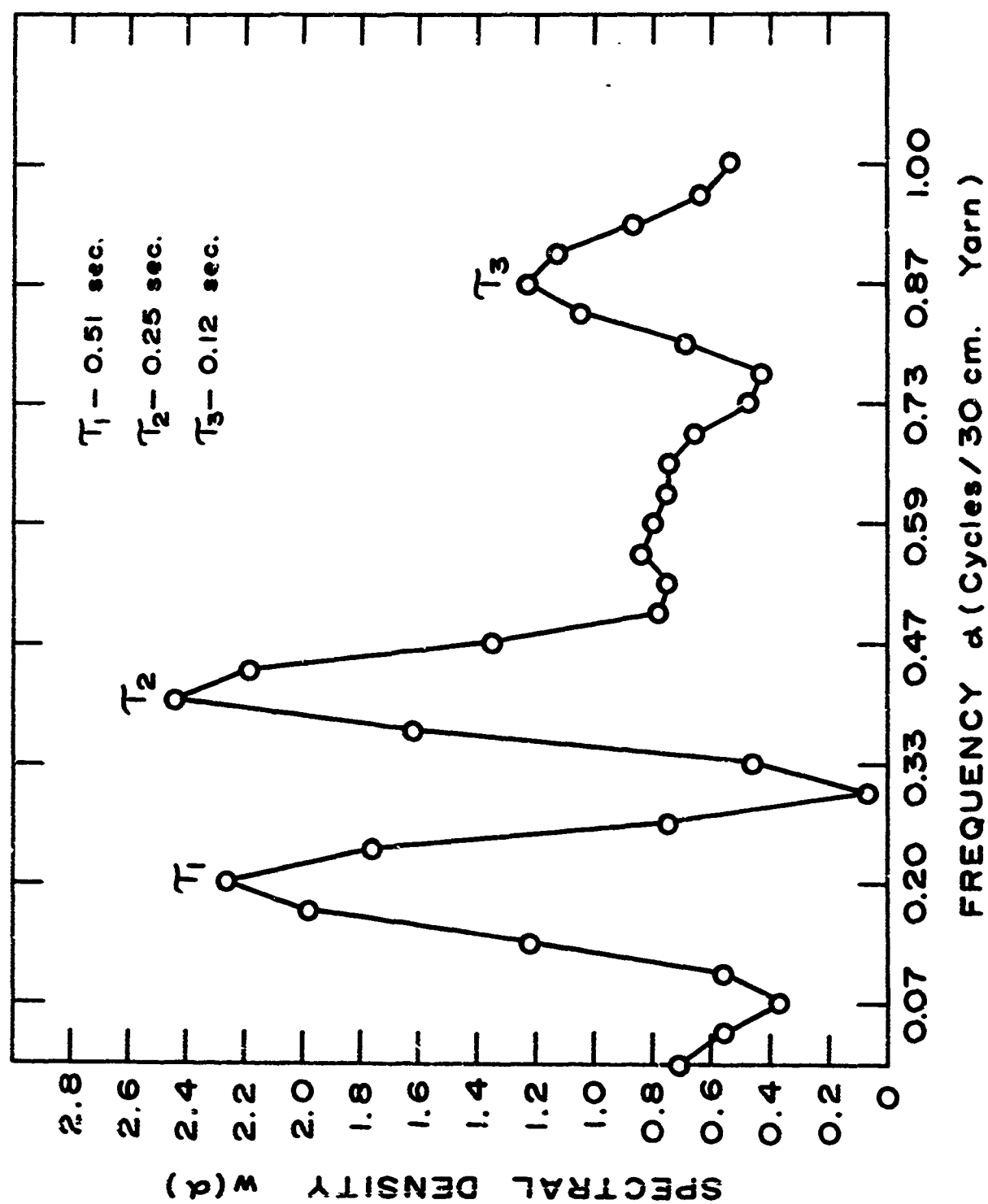


FIGURE 5

experimental precursor yarn to a structure which when finally drawn yielded a strength of 10-12 grams/denier. The oscillatory structure of the correlogram and level of the power spectrum indicate features of simple autoregressive processes. However, the "peaks" in the latter appear to arise from a more determinate oscillation. The referenced paper suggests that these may arise from disturbances acting on the molten thread line.

Mechanical models are available to explain certain observed features of these oscillations. The nonlinear oscillations of the molten thread line first studied by Spangler as reported by Busse and Oplinger. These models envision relaxation triggered disturbances exciting the molten thread line. Approximate equations for the behavior of the thread line have been developed by Oplinger. The basic equation is nonlinear, but can be separable into two wave-like equations which are coupled through the given relaxation properties of the thread line. Such solutions involve elliptic trigonometric functions which behave over a useful range of the arguments very much like trigonometric functions commonly used to describe simple waves. The solution of this wave equation contains an observed feature of the thread line oscillations, namely that the higher the observed frequency (resonance) the lower the lower bound to the tension amplitude.

A simpler form of this nonlinear oscillation is discussed by Lee. In contrast with the work of Oplinger, this author uses elastic string theory and develops the nonlinearity in terms of the tension acting in the string. As the transverse displacement increases the restoring forces arising from the tension increase in a nonlinear fashion. The lower bound to the oscillation amplitude is essentially constant and the upper bound rises with increasing frequency. The work of Lee reduces to the theory of Carrier for stretched strings exhibiting free rather than

forced vibrations. The Lee work has the merit of being dependent upon simple trigonometric functions rather than the elliptic functions which arise from Oplinger's solution.

Certain of characteristic frequencies observed in the spectral analysis of the denier fluctuations may find explanation in oscillations of the type discussed by Oplinger. It should be noted that his treatment assumes a complex relaxation process which in a linear approximation contains a viscous element with both an instantaneous modulus and a "relaxed" modulus.

The origin of the nonlinear oscillation might well involve a relatively sharp strain change consequent to axial elongation of the type discussed above and originally suggested in another context by Flory. The details of the quenching system would presumably describe the transverse loading required to make the Oplinger analysis at least qualitatively valid.

In any event, one or both the mechanisms suggested above may be invoked to lend physical plausibility to the denier fluctuations analyzed in the work undertaken as part of the instant project. Only future research will reveal the validity of the plausibility arguments presented here.

Evidence of Microfibrillar Character of Melt Spun Polypropylene Fiber

(P. A. Tucker, Jr., Graduate Student)

Filaments taken from the Roper-George study of precursors of strong polypropylene fiber were "peeled" using a technique described by Scott. The resulting fiber sections were then examined, after coating with Au in the usual manner, in a scanning electron microscope. (The technique of preparation and a more complete discussion will appear subsequently.) A typical section showing

the peel is shown in Figure 1. Figure 2 shows a transverse section at a higher magnification (X35,000). The interconnecting microfibrils visible here are reminiscent of those shown by Keith et al. and Williamson and Busse in polyethylene films.

The existence of these microfibers in the fine structure of oriented polypropylene fiber is a new observation. Possibly, these regions represent the locus of an essential interconnection between the more or less oriented microfibrils. As such, strength of the bundle would clearly be a function of the properties of the interconnecting microfibrils.

One brief study has been made of the nature of the microfibrils visible in Figure 3. These regions, after splitting the filament, have been subjected to nitric acid and Br_2 gas under conditions of photolytic addition of Br to unsaturated ($-\text{C}=\text{C}-$) carbon bonds. The former materials at -20°C to -60°C etch away the microfibrils in times ranging from $1/2$ to several hours. The latter, at room temperature, similarly results in the complete removal of the visible microfibrils. The former result in accordance with the results of workers previously cited. The latter, Br_2 gas, result is new. This result suggests that the microfibril is in some way essentially labile to the halogen and/or the environmental $h\nu$ used to trigger the reaction, and somewhat less to the strong mineral acid. The electron diffraction pattern obtained by Padden for a polyethylene microfibril (transmission) suggested that the structures seen by him are quite stable, highly ordered extended chain polyethylene crystal.

The microfibril observed in the case of the polypropylene melt spun fiber is worthy of further study - it is the subject of Mr. Tucker's dissertation.

Strength of a Filament as Determined by the Microfibrillar Bundle

(Dissertation of Dr. Moon Suh)

Suh, and Suh and George, have discussed a second major study undertaken in connection with the subject project. The problem formulated describes the failure of a bundle of parallel elements under the assumption of equal extension of the elements with strength distributed in accordance with a known probability distribution function. The failure of the elements at a given load and bundle extension is independent one from the other. For this case closed form formulae are obtained for all the moments of the bundle of n elements. Finally, these moments are deduced for the limit of $n \rightarrow \infty$. If the probability of an element of unit length failing between extension l and $l + \delta l$ is known, all remaining moments can in principle be computed. Such computations are quite detailed and have only been carried out for small values of n and the asymptotic form indicated for simple elementary probability functions. These are found in the references cited.

A class of inequality relations for the expected strength of bundles of n size and $m \leq n$ filaments were discovered in connection with the above statistical studies. These enable one to bound the strength properties of a given bundle in terms of those of a very large ($n \rightarrow \infty$) bundle and smaller bundle with known properties. These inequalities are,

$$E \left(\frac{B_n}{n} \right)^k \leq E \left(\frac{B_m}{m} \right)^k \quad \text{for } 1 \leq m \leq n$$

$$k = 1, 2, 3, \dots$$

$$x_0^k [1 - F(x_0)]^k \leq E \left(\frac{B_n}{n} \right)^k \leq E (B_1)^k$$

$$k, n = 1, 2, 3, \dots$$

In the above, if $k \equiv 1$, $E\left(\frac{B_n}{n}\right)$ is the expectation of the strength (first moment) for the bundle of n filaments, $B_1(x)$ is the conditional probability that a single filament will hold at or below the load x . The inequalities, depending upon the form of $B(x)$, offer estimates of practical bounds to the strength of a given bundle.

The monotonicity in the reduction of the performance of the bundle with each added element in the parallel provides a strong theoretical stimulus to search for models of strength wherein the array of added elements assume a lesser role in decreasing the bundle strength. Future work in this direction is indicated.

Concluding Remarks

The instant project was terminated one year short of its planned duration. Because of this, it is difficult to package the work in closed form. It is clear that the strength elements within a fiber may be taken as a bundle of nearly parallel microfibrils. The necessity of this viewpoint remains to be established.

If the strength elements are microfibrils, it is clear from the electron microphotographs that nature provides some way or set of ways in which they are interconnected. Thus, even if, as is highly likely, the strength of a mean fibril is statistically distributed for any given loading epoch [degrees of dynamic effect are envisioned here, each with its characteristic $B_n(x)$], it is certain that one will need a cooperative theory of some sort to account for the nature of the interaction.

The interaction may well change with the dynamic nature of the load application. The point of view adopted by George and Chou can be extended to other types of materials response. The suggestion that the "tie points" are loci

of metastable one-dimensional dislocations allows the stability to change with the time scale of the loading epoch. The reaction of the "tie points" under dynamic load then provides a fertile concept for exploring dynamic materials response phenomena.

The interconnecting "transverse" microfibrils can serve to delimit the effective length of the set of axial microfibrils. The shorter this effective element the generally higher level of strength the set will exhibit. Such effects may be expected in conditions of the response of the macrofibrillar structures to a dynamic application of traction. Alternatively, the interconnections may generally be expected to reduce the general inefficiency of the bundle. This would follow by permitting the interconnected bundle of n filaments to behave like a bundle of substantially smaller size $m < n$, which is otherwise more efficient in accepting load levels comparable to the modal properties of the single filament, $B_1(x_0)$.

We see thus that the presence of interconnections between the axial elements of the macrofiber, together with the theoretical model of parallel elements with properties statistically independent of each other allows one to envision both dynamic strengthening and embrittlement of the real structure. The point of emphasis for future work is clearly evident.

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APPENDIX

TENSILE FAILURE OF BUNDLES OF NEARLY PARALLEL FILAMENTS*

Paul A. Tucker, Jr., Bala Batavia and Waller George

Abstract

One commercial polypropylene yarn and two experimental yarns of intermediate strength have been used to study the failure mechanics of nearly parallel bundles loaded at constant rates of extension. For sufficiently low rates of extension, the bundle breakdown is observed to proceed by the successive rupture of component filaments as the remaining bundle elements collectively sustain increasing extension. Two general patterns of failure are observed in the experimental yarns. One typical pattern involves substantial numbers of filaments which fail at an over-all extension which is large as compared with the extension at failure of the component single filaments measured under comparable loading conditions. A similar behavior is found in the case of a commercial carpet yarn. The second typical failure pattern also involves progressive rupture, but over a relatively restricted region of bundle extension which, while somewhat larger, is more comparable with the single filament extension at failure.

The two modes of failure are characterized in terms of the pattern of mean load per filament on remaining filaments as the bundle breakdown progresses. The different failure modes are related to variability in filament lengths and alignment within the bundle, as well as variations in filament properties among other factors. The development of interfiber forces transverse to the axis of the imposed extension is discussed as a requirement for enhancement of bundle extensibility over the inherent single fiber breaking extension.

* Presented at the Synthetic Fiber Symposium, Williamsburg, Virginia, April 19-21, 1968.

STATISTICAL NATURE OF BREAKAGE IN BUNDLES^{xx}

Moon Won Suh and Waller George

Abstract

For a bundle of filaments which are parallel, of equal length and gripped at their ends, the probability distribution of bundle strength is obtained as a function of the strength distribution of the constituent filaments. The breakage model is based on the postulates that the load in a filament increases along with the increase in its extension up to the point of breakage, and that the bundle load at any given extension is uniformly distributed among the surviving filaments.

Defining the strength of a bundle as the maximum load attained in the bundle throughout its load-extension history to the final filament break, the distribution function of bundle strength with n filaments, $S_n(x)$, can be expressed in terms of $S_{n-1}(x)$, $S_{n-2}(x)$ and $F(x)$ that is the distribution function of filament strength as:

$$S_n(x) = \sum_{k=1}^n (-1)^{k+1} \binom{n}{k} \left[F\left(\frac{x}{n}\right) \right]^k S_{n-k}(x)$$

The asymptotic properties for the strength of a large bundle are deduced utilizing several measure theoretic modes of convergence and the results indicate that $\frac{B_n}{n}$, the bundle strength divided by the number of filaments in the bundle, obeys asymptotically, a normal distribution with mean and variance $x_0 [1 - F(x_0)]$ and $\frac{1}{n} x_0^2 F(x_0) [1 - F(x_0)]$, respectively, where x_0 is the value of x which maximizes $x [1 - F(x)]$. Though this result confirms the validity of an earlier work of H. E. Daniels [Proc. Roy. Soc. (London), 83.405 (1945)], the formulation of the present study is distinct and simpler compared with the lengthy and complex work of Daniels. The use of the asymptotic forms of Daniels in the analysis of fracture mechanics in composite structures will be reexamined relative to the results obtained here.

The second part of the paper is devoted to the proof of a number of moment inequalities that are useful in comparing the efficiencies of two bundles with different number of filaments. Upper and lower bounds of $E \left(\frac{B_n}{n} \right)^k$ are obtained, viz:

$$E \left(\frac{B_n}{n} \right)^k \leq E \left(\frac{B_m}{m} \right)^k \quad \text{for } 1 \leq m < n$$

$k, m, n = 1, 2, 3, \dots$

^{xx} Presented at the Fourth Annual Symposium on High Performance Composites, St. Louis, Missouri, April 7-10, 1969.

$$x_0^k [1 - F(x_0)]^k \leq E \left(\frac{B_n}{n} \right)^k \leq E (B_1)^k = E (X^k)$$

$$k, n = 1, 2, 3, \dots$$

where X is the filament strength.

In the last part of the paper, the effect of filament length on bundle strength is examined. By extending the weakest-link theory of filament strength to the breakage of a bundle, the changes brought about in distribution and asymptotic behavior of a large bundle are evaluated with respect to the uniform changes of filament length within the bundle. Also, an important probability inequality is established for comparing the length effect in a bundle with that in a single filament.

A STUDY OF THE DISTRIBUTION AND MOMENTS OF BUNDLE STRENGTH IN SEQUENTIAL BREAKAGE OF PARALLEL FILAMENTS*

Moon Won Suh

Abstract

For a bundle of filaments which are parallel, of equal length and gripped at their ends, the statistical nature of breaking strength is studied based on two models of bundle breakage.

The restricted model is based on the postulates that the load in a filament increases along with the increase in its extension, and that the load in a bundle at any given extension is equally shared by the surviving filaments at the extension. Defining the bundle strength as the maximum load attained in the bundle throughout its load-extension history to the final filament break, the distribution function of bundle strength is obtained as a function of the distribution of filament strength by a probabilistic argument of events associated with bundle breakage.

The asymptotic properties for the strength of a large bundle are deduced utilizing several measure theoretic modes of convergence and the results indicate that the bundle strength divided by the number of filaments in the bundle, $\frac{B_n}{n}$, converges in probability to a constant and tends to obey, asymptotically, a normal distribution with mean and variance determined from the underlying distribution of filament strength. Though the results confirm the validity of an earlier work, the formulation of the present study is distinct and simpler.

The next part of this study is devoted to the proof of a number of moment inequalities that are useful in comparing the efficiencies of bundles which differ in their number of filaments. It is shown that every moment of the random variable, $\frac{B_n}{n}$, monotonically decreases as n increases, and it has a lower bound which coincides with its limit. The lower bound is determined from the distribution of filament strength as well as the order of the moment. The same monotonicity property is proved for a finite population of filaments by defining the moments under the scheme of simple random sampling.

The effect of filament length on bundle strength is examined by generalizing the weakest-link theory of filament strength to the breakage of a bundle. The

* A thesis submitted to the Graduate Faculty of North Carolina State University at Raleigh in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, 1969.

changes brought about in distribution and asymptotic behavior of a large bundle are evaluated with respect to the uniform changes of filament length within the bundle. Also, the probability of strength retention is obtained for a bundle of n filaments in which the filament lengths are uniformly augmented.

Finally, an alternative model for bundle breakage is proposed in order to relax one of the postulates given in the restricted model. By assuming that the load in a filament is a random variable functionally dependent on its extension, the mean and variance of bundle strength are approximated by use of the distribution of bundle load definable at any given extension.

STRONG POLYPROPYLENE FIBER: PROCESSES FOR ITS PRODUCTION*

James Roper and Waller George

Sheehan, et al. [1] have discussed an extrusion process for the production of high tenacity polypropylene filaments. In essence, they preferred a production scheme which involves extrusion from a relatively high melt temperature followed by gravitational attenuation (down extrusion). The attenuated product was taken up on an intermediate package. A second stage of the process involves hot drawing, preferably with a prior annealing. Tenacities somewhat in excess of 12 gpd (8 - 20 percent elongation) were achieved in monofilaments which were further annealed, redrawn, and then finish annealed to homogenize the otherwise somewhat overdrawn structure. The process favored polymers characterized by a low melt index (high molecular weight) preferably between 0.8 and 2.0.

It is the purpose of this letter to reveal another, essentially different, process route for the production of high tenacity polypropylene fiber and yarn. It uses extrusion equipment similar to that utilized by Sheehan, et al. An essential feature of this process is the maintenance of melt temperatures between 250 and 285° C. The lower melt temperature assists the production of a metastable, ordered structure termed "paracrystalline" by previous workers [1], which is highly desirable as a precursor to final ordering by high drawing. The demands placed upon the polymer melt stabilizers are concurrently minimal. Conventional extrusion is followed by gravitational attenuation of approximately 12X followed immediately (without intermediate packaging) by "in-line" drawing between 4X - 6X. A third cold godet is introduced with a slight relaxation to guarantee a retention of the orientation for a longer period of time before relaxation of the threadline tension and take-up on a conventional winder tube. With this "in-line" drawing it has been possible to produce a precursor yarn (7-filament 200 - 300 denier) which with a light second stage drawing readily produces 10 gpd (20 - 25 percent elongation) material from substantially lower molecular weight polymer, e.g., 5, and 12 melt index.

The second essential feature of the instant process is the introduction of substantial levels of orientation in the fiber before relaxation of threadline tension and take-up onto an intermediate package. The limiting feature of this process is the extent of the in-line drawing step and the subsequent take-up of the incompletely drawn product.

Preheat at the position of the first godet seen by the yarn at the end of the attenuation stage is helpful in increasing the in-line draw ratio. The temperature of the first godet is adjusted to be as high as practicable for linear input

*To be published.

speed (as required by the attenuation stage) of approximately 50 meters/min. The yarn is wrapped on the godet and idler roll four to eight times and then passed to a second draw roll introducing between 4X and 6X draw. The process tends to be inoperable for draws of around 6X for polypropylenes of U. S. commercial quality with a melt index between 5 and 12.

The hot surface used in connection with the final draw is maintained near the "stick" temperature, and the yarn is held through multiple wraps on the surface of rolls at 135° C prior to passage over the (about 150° C) draw plate. Quenching is delayed during draw by maintaining the second godet at approximately 125° C with 4 to 8 wraps followed by a very slight reduction of the in-line tension to a quenching godet operating at about 30° C. Final cooling of the threadline occurs as the yarn is passed through a traveler onto the bobbin.

The parent yarn used in this study is characterized by a geometrical filament length irregularity which results in length differences of the order of a few mm in 10 meter lengths of product. The "long" length is produced statistically at each of the seven holes in the spinnerette with what appears to be equal probability over relatively long periods of extrusion (hours). This "loopiness" in the yarn results in a local dancing of the wraps as the yarn passes along the idler roller and from godet to godet. This length irregularity is one stochastic aspect of the extrusion process which is the subject of a forthcoming paper by one of us (W. G.). One consequence of this length variability in the "as-extruded" and drawn product is that the 7-filament yarn exhibits variable strength properties along its length. The pattern of property variability along the yarn can be analyzed as a time series to yield evidence of the stochastic nature of the extrusion process. Individual test results, treated as a group sample, reveal a surprising feature of the variation of the strength of this yarn shown in Figure 1. Here is plotted the ultimate tenacity of the yarn (measured for 10 inch, 7-filament, yarn specimens conditioned to 70° F. 65 percent R.H., using the Instron tester with crosshead speed of 6 in./min) as a function of the yarn elongation at the point of initial failure (the first of the 7 filaments). It is evident that the in-line orienting process with its "delayed quench" feature produces a product with a local strength which increases monotonically with tensile elongation. It is tempting to suggest that within the stochastic variability noted above that regions of higher orientation are associated with regions of higher ultimate strength and associated higher elongation. Regardless of the orientation fluctuation which may or may not be present in the yarn, the example reported here is of interest as a process for the production of very high tenacity fiber. Other systems are known which produce materials which exhibit high dynamic performance, wherein the ultimate strength and the ultimate ductility (elongation) increase together. For example, the magnesium aluminum rich alloys known as "hydroaluminum" in England and S56 in the United States are known to exhibit this feature. The strength in this case is in part controlled by cold and "cool" working processes.

Several years ago Rosenthal [2] introduced a factor, F , which empirically rates the strength potential of a wide range of materials. He defined this factor as

$$F = T : E^{1/2}$$

where T is the tenacity or the ultimate strength of the material per unit weight, and E the elongation at the ultimate tenacity. The higher factor F , the higher strength potential of the material.

Using Rosenthal's F factor, the potential strength of strong polypropylene filaments disclosed in Sheehan's work appears to be between 30 and 40 gpd. Typical values of the Rosenthal factor for the strong polypropylene yarns discussed above average in excess of 45 with occasional values (one out of five) as high as 65. Comparison of these latter numbers with those obtained from Sheehan's work suggests that the fibers produced by the process disclosed herein do in fact represent a material with a strength potential which is roughly twice that previously reported.

Sheehan's data on supertenacity polypropylene was confined to single filaments. The values reported here are for a small bundle tested at a rather long gauge length without the benefit of twist or a high rate of elongation. The detailed testing conditions for Sheehan's data are not reported. However, Laible [3] shows for large yarn bundles that roughly 1 gpd increase can be expected in changing testing conditions twelvefold from 10 percent/min to 240 percent/min. If Sheehan's data represent typically slow testing conditions, his process is then possibly capable of producing stronger yarn than that reported here. However, it appears likely that the instant results represent essentially comparable testing conditions. Single filament test results tend to be higher than bundle results. A comparison of the observed yarn strength levels (contrasted with estimates of strength potential) reported here with those of Laible show the instant yarn is substantially stronger than that used in his survey of 1964.

The apparent relationship defined by the points plotted in the figure suggests the higher yarn tenacities in general should be correlated with material possessing higher over-all elongation. Fibers produced by Sheehan and referred to above do not exhibit the relationship shown in Figure 1. In general, for Sheehan's filaments, an inverse or monotone decreasing relationship is found suggesting that the higher tenacities were achieved primarily at the expense of ductility (tensile elongation). If the second stage of drawing in our "delayed quench" process is permitted to impose draw ratios sufficiently high to produce internal disruption during the drawing, like Sheehan we find tenacity is produced at the expense of elongation. We have not, as yet, attempted to "heal" these internal voids.

Currently, others within the school are examining the microfibrillar character of the fiber described above. Finally, it may be noted that this strong fiber can be further drawn by conventional draw stages to yield tenacities of the order of those found by Sheehan (up to 13 gpd) with an attendant reduction of tension elongation to levels of 10 to 12 percent.

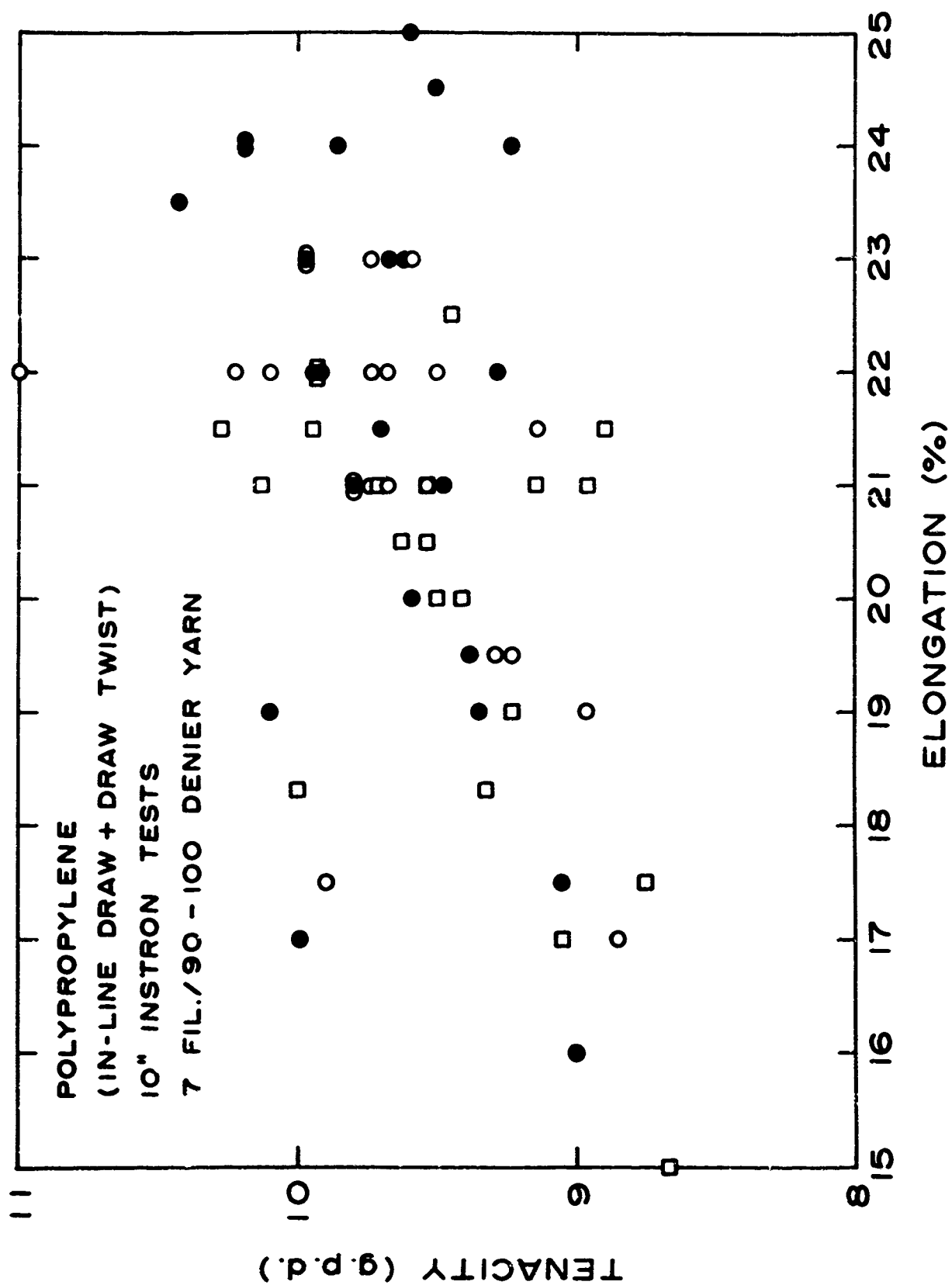


FIGURE 1

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INHOMOGENEOUS DEFORMATION OF NYLON 6,6^{*}

Yeun-Jong Chou

Abstract not available.

^{*} A thesis (now in rough draft form) to be submitted to the Graduate Faculty of North Carolina State University at Raleigh in partial fulfillment of the requirements for the Degree of Master of Science.

THE MECHANO-CHEMISTRY OF NYLON 6,6 FIBER YIELD POINT*

T. Waller George and Yeun-Jong Chou

Abstract

Metal physicists have suggested two mechanisms to account for the yield point phenomena in metal crystals (e. g., carbon steels). An early suggestion was that of Cottrell which envisioned dislocation networks "pinned" prior to the yield point. More recently the "Cottrell mechanism" has been replaced in part by suggestions of Gilman and Johnston who envision after an appropriate delay time the local release of mobile dislocations under the action of the imposed stress. The release of the dislocation array is characterized by the lower yield point.

The yield point in nylon 6,6 bulk samples and film has been shown by Miklowitz and Kauffman and George to operationally resemble that in metals. Data due to Woods, Hookway and Quynn on the effects of small molecules such as alcohols, glycols, chloroform, saturated hydroxy compounds and chlorinated hydrocarbons are reexamined with regard to the reactions of these compounds with the undrawn nylon 6,6 fiber. These compounds alter the character of the ambient yield point. Those showing the greatest reduction in yield point also reduce the delay time for yielding. No compounds are known which raise the yield point in nylon 6,6 (water does in the natural Ramie fiber). Significant differences exist in the capacity of the OH containing compounds to reduce or remove the yield point. These differences are discussed in terms of the more chemically accessible regions of the fiber. The hydrocarbon moiety in compounds which tend to complex with the amide group in the polymer chain appears to effect the efficiency of the stress released dislocations in reducing or removing the yield point. Therefore, it is suggested that such factors are of importance in determining the mechanical reactions of the para-crystalline (less well developed ordered regions) of the nylon 6,6 fiber. Thus, at ambient conditions ethyl alcohol does not "loosen" the accessible, amorphous, nylon 6,6 structure as effectively as methyl alcohol and both are less effective than water.

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13. ABSTRACT - The report outlines research undertaken to identify a set of microstructure elements present in strong organic fiber in which reside the primary means of response on the part of the material to dynamic load application. The elements involve two microfibrillar concepts, viz., a set of nearly parallel structures and a set of finer transition fibrils which bridge between the former under conditions of nearly axial alignment. Scanning electron micrographs of the structural features are reported. The transition fibril is reported in one experimental setting to exhibit evidences of a labile chemical structure under exposure to ultraviolet radiation in the presence of halogens (room temperature). A second principal contribution involves the statistical theory of the strength of a parallel array of fiber. The model envisions individual filaments possessing strength properties distributed along the length in accordance with the conventional weakest-link hypothesis. A set of moment inequalities has been obtained which shows the mean bundle strength per element in the absence of interaction between the constituent elements to be progressively degraded as the bundle size increases. A finite asymptotic limit is obtained as the number of elements approaches infinity. Similar inequalities and limits have been obtained for higher moments of the underlying distributions describing bundle strength. Physical evidence of tie elements suggests the need for statistical studies of bundles containing interaction between elements.		

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